CHEM 371. PROBLEM SET 1. DUE JAN. 23, 2020.

(1) Consider a system of 5 distinguishable spins in the absence of an external field (each spin being able to point up or down.) If a movie were taken of this system in equilibrium, what fraction of the movie frames would show *n* spins pointing up? Consider all possible values of *n*, viz., *n* = 0, 1, 2, 3, 4, 5.

(2) A box is separated by a partition that divides its volume in the ratio 3:1. The larger portion of the box contains 1000 molecules of Ne; the smaller contains 100 molecules of He. A small hole is made in the partition and the system is allowed to settle into a state of equilibrium.

(a) Find the average number of molecules of each type on either side of the partition.

(b) What is the probability of finding 1000 molecules of Ne in the larger portion and 100 molecules of He in the smaller portion (i.e., the same distribution as in the initial system)?

(3) Suppose you have *n* dice, each a different colour, all unbiased and 6-sided.

(a) If the dice are rolled all at once, how many distinguishable outcomes are there?

(b) Given 2 distinguishable dice, what is the most probable sum of their face values on a given throw of the pair?

(c) What is the probability of the most probable sum?

(d) If a fair 6-sided die is rolled 3 times, (i) What is the probability of getting a 5 twice from all three rolls of the die? (ii) What is the probability of getting a total of at least two 5's from all three rolls of the die?

(4) A system is composed of 2 distinguishable harmonic oscillators, each of frequency ω and each having permissible energies $(n+1/2)\hbar\omega$, where *n* is any non-negative integer. The total energy of the system is $E' = n'\hbar\omega$, where n' is a positive integer.

(a) How many microstates are available to the system? What is the entropy of the system?

(b) A second system is also composed of 2 distinguishable harmonic oscillators, each of frequency 2ω. The total energy of this system is $E'' = n''\hbar\omega$, where n'' is an even integer. How many microstates available to this system? What is the entropy of this system?

(c) What is the entropy of the system composed of the two preceding subsystems (separated and enclosed by a totally restrictive wall)? Express the entropy as a function of E' and E''.

(5) A system is composed of 2 harmonic oscillators of frequencies ω and 2ω, respectively. If the system has total energy $E = (n+1/2)\hbar\omega$, where *n* is an odd integer, what is the entropy of the

system? If a composite system is made up of two non-interacting subsystems of the type just described, having energies E_1 and E_2, what is the entropy of the composite system?

(6) One kg of water, initially at equilibrium at 20 °C, is heated to 100 °C, and left in an insulated container, again at equilibrium. Calculate the ratio of the number final microstates Ω_f to the number of initial microstates Ω_i. That is, find Ω_f/Ω_i.

(7) Show, starting from Newton's law in one dimension, $F = ma$, that the law can be written in Lagrangian form,

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{d\dot{x}} - \frac{\partial \mathcal{L}}{\partial x} = 0$$

where $\mathcal{L} = K - V$, with K the kinetic energy and V the potential energy. State the assumptions, if any, that you make in your derivation.

(8) Show that Euler's equation $\frac{\partial f}{\partial x} - \frac{d}{dt}\frac{\partial f}{\partial \dot{x}} = 0$ is equivalent to

$$\frac{\partial f}{\partial t} - \frac{d}{dt}\left(f - \dot{x}\frac{\partial f}{\partial \dot{x}} \right) = 0$$

(9) Show that if the Lagrangian of a particle is given by

$$L = mc^2\left(1 - \sqrt{1 - \frac{\mathrm{v}^2}{c^2}}\right) - V(\mathbf{r})$$

where m is the mass of the particle, $\mathbf{r}$ its position, $\mathbf{v}$ its velocity, $V(\mathbf{r})$ the potential energy and c the speed of light, then the particle obeys the following relativistic form of Newton's second law:

$$\frac{d}{dt}\left(\frac{m\mathrm{v}_i}{\sqrt{1 - \mathrm{v}^2/c^2}} \right) = F_i$$

where v_i and F_i are, respectively the ith component of the velocity and force.

(10) (i) Show that the integral $J = \int_{t_1}^{t_2} dt\, g(y, \dot{y}, t)$ with $g = y(t)$ has *no* extreme values.

(ii) Show that if a function f is defined as $f(y, \dot{y}, t) = f_1(y, t) + \dot{y} f_2(y, t)$, then the extremization of the integral $I = \int_{t_i}^{t_2} dt\, f(y, \dot{y}, t)$ leads to the condition $\frac{\partial f_1}{\partial y} - \frac{\partial f_2}{\partial t} = 0$.